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(74) Agents: MARIN, Mark, D. et al.; ExxonMobil Research
and Engineering Company, 1545 Route 22 East, P.O. Box
900, Annandale, NJ 08801-0900 (US).

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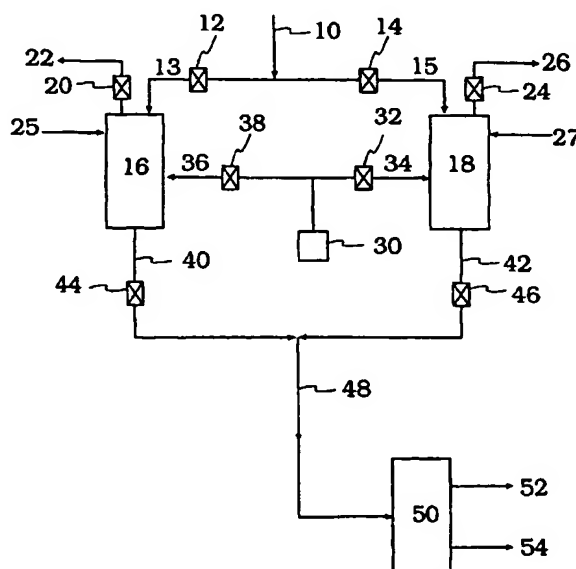
(71) Applicant: EXXONMOBIL RESEARCH AND ENGI-
NEERING COMPANY [US/US]; 1545 Route 22 East,
P.O. Box 900, Annandale, NJ 08801-0900 (US).

(72) Inventor: JIANG, Zhaozhong; 25 MacIntosh Road,
Somerville, NJ 08876 (US).

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(54) Title: ENHANCED LUBE OIL YIELD BY LOW OR NO HYDROGEN PARTIAL PRESSURE CATALYTIC DEWAXING
OF PARAFFIN WAX



(57) Abstract: Catalytic dewaxing of paraffin containing feeds with a catalyst having a certain pore structure, where the feeds are preferably produced from syn gas using a non-shifting Fischer-Tropsch catalyst, is accomplished in the substantial absence of added hydrogen, and a cyclic isomerization - catalyst regeneration process is provided.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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**ENHANCED LUBE OIL YIELD BY LOW OR NO HYDROGEN
PARTIAL PRESSURE CATALYTIC DEWAXING OF PARAFFIN WAX**

FIELD OF THE INVENTION

[0001] This invention relates to a process of catalytically dewaxing paraffin containing hydrocarbons. More particularly, this invention relates to the production of lube base oils and diesel range oils with a pre-determined or pre-selected pour point or cloud point by catalytic dewaxing in the substantial absence of added hydrogen, at low or no hydrogen partial pressures.

BACKGROUND OF THE INVENTION

[0002] , There is a need for high quality products having a relatively high boiling point, such as lube base oils and diesel range oils, with low pour and cloud points. The production of lube base oils and diesel range oils by the hydroprocessing of paraffin containing feeds is well known, e.g., hydroisomerization or hydrocracking of the paraffin feed. The processes are generally catalytic and are usually carried out at relatively high hydrogen pressures, e.g., >500 psi (3448 kPa) hydrogen partial pressure. Catalytic dewaxing is a form of hydroprocessing and involves paraffin isomerization and some hydrocracking. Dewaxing of paraffin containing feeds serves to decrease their pour and cloud points, mainly by isomerization of n-paraffins. Hydrocracking, however, is generally undesired in a dewaxing process, because it leads to low boiling, low viscosity, low value products such as short chain hydrocarbons, e.g., C₁-to C₄ hydrocarbons.

[0003] Hydrogen has always been used in catalytic dewaxing mainly for promoting extended catalytic life by, e.g., reductive coke removal, see U.S. 4,872, 968. Hydrogen partial pressures in catalytic dewaxing ranges from about

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200 psig (1480 kPa) to about 1,000 psig (6996 kPa) or more, e.g., see U.S. 5,614,079, and hydrogen partial pressures are usually in the higher end of the range for reasons of catalyst life.

[0004] U.S. 5,362,378 discloses hydrogen partial pressures ranging from 72 to 2,305 psig (598 to 15994 kPa) for use with the large pore catalyst zeolite beta. This patent does not mention catalyst life or TIR, i.e., temperature increase required, necessary for maintaining product specifications, such as pour point or cloud point. Large pore zeolite beta is typically not classified as a dewaxing catalyst, but as an isomerization catalyst, and products produced utilizing such catalysts in accordance with U.S. Patent 5,362,378 would need to be dewaxed in order to achieve the low pour and cloud points obtained from the instant process.

[0005] It was the object of the present invention to provide for a process that will increase the yield of product with high boiling point, but low pour and cloud point. In other words, the process should have little or no hydrocracking. In particular, there is always a need for a process that will produce lube oils with high boiling point, high viscosity, and low pour and cloud points.

[0006] We have now found that a particular combination of features allows for conducting catalytic dewaxing in the substantial absence of added hydrogen, at low or no hydrogen partial pressure, and conditions that are selective to hydroisomerization with little or no hydrocracking. Surprisingly, the process of the invention allows for the decrease of the pour or cloud points of a feed, while maintaining the high (kinematic) viscosity, and all of this with a high yield.

SUMMARY OF THE INVENTION

[0007] The invention relates to a catalytic dewaxing process which comprises reacting a paraffin containing feed stock over a catalyst comprising a molecular

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sieve with a one dimensional pore structure having an average diameter of 0.50 to 0.65 nm, and a metal dehydrogenation component, at dewaxing reaction conditions and in the substantial absence of added hydrogen.

[0008] In a preferred embodiment of this invention, a paraffin containing feed, preferably a feed containing at least 80 wt% n-paraffins, is catalytically dewaxed in the presence of a molecular sieve catalyst with one dimensional pore structures having an average diameter of 0.50 nm to 0.65 nm, and the difference between the maximum diameter and the minimum diameter is preferably ≤ 0.05 nm. The molecular sieve is exemplified by, for example, ZSM-23, ZSM-35, ZSM-48, ZSM-22, SSZ-32, zeolite beta, mordenite and rare earth ion exchanged ferrierite in conjunction with a dehydrogenation component. Preferably the molecular sieve catalyst is ZSM-48 (ZSM-48 zeolites herein include EU-2, EU-11 and ZBM 30 which are structurally equivalent to ZSM-48) with a dehydrogenation component; and the process is carried out in the substantial absence of added hydrogen.

[0009] By substantial absence of added hydrogen is meant the only added hydrogen will be that which is inherently present in the feeds. In a preferred embodiment, the amount of inherent hydrogen in the paraffin containing feed is the amount that is present in a Fischer Tropsch hydrocarbon fraction. Such fraction is usually obtained by distillation, which distillation substantially removes dissolved gasses, and the amount of inherent hydrogen in the paraffin containing feeds is then the amount which is physically adsorbed by the liquid or waxy Fischer Tropsch hydrocarbon fraction.

[0010] When hydrogen is present during the reaction, either as a consequence of the reaction or as inherent hydrogen, the hydrogen partial pressure is preferably less than 100 psig (791 kPa), more preferably less than 70 psig (584 kPa).

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[0011] In another embodiment of this invention, the catalyst is stable, that is, it can meet a predetermined pour point for at least two weeks.

[0012] In yet another embodiment of this invention, a cyclic process is provided wherein catalytic dewaxing occurs in a first zone while in a second zone catalyst is regenerated or rejuvenated, after which the feed is switched to the second zone where catalyst has been regenerated and the catalyst in the first zone is regenerated. Thus, a continuous catalytic dewaxing process may be provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figure 1 is a schematic of a cyclic isomerization – catalyst regeneration process.

[0014] Figure 2 is a plot showing the effect of hydrogen pressure on lube yield for isomerization of a Fischer-Tropsch wax over Pt/ZSM-48. Pour point ($^{\circ}\text{C}$) is on the abscissa and wt% on feed $700^{\circ}\text{F}+$ ($371.1^{\circ}\text{C}+$) lube yield is on the ordinate. The lines A, B, C, and D denote the results of processes that were run with varying amounts of added hydrogen, i.e., hydrogen partial pressures of 1000 psig (6996 kPa), 500 psig (3549 kPa), 300 psig (2170 kPa), and 0 psia (0 kPa, no (added) hydrogen), respectively.

[0015] Figure 3 is a plot showing the effect of hydrogen pressure on gas yield for isomerizing a Fischer-Tropsch wax over Pt/ZSM-48. $700^{\circ}\text{F}+$ ($371.1^{\circ}\text{C}+$) lube pour point ($^{\circ}\text{C}$) is on the abscissa and is plotted against wt% on feed $\text{C}_1\text{-C}_4$ gas yield on the ordinate. Lines A, B, C, and D denote the results of processes that were run with varying amounts of added hydrogen, i.e. hydrogen partial pressures of 1000 psig (6996 kPa), 500 psig (3549 kPa), 300 psig (2170 kPa), and 0 psia (0 kPa, no (added) hydrogen), respectively.

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[0016] Figure 4 is a plot showing the effect of hydrogen pressure on lube viscosity for isomerization of a Fischer-Tropsch wax over Pt/ZSM-48. Pour point (°C) on the abscissa is plotted against kinematic viscosity @ 100°C in centistokes (cSt) on the ordinate. Lines A, B, and C denote 0 psia, 500 psig (3549 kPa), and 1000 psig (6996 kPa), respectively.

[0017] Figure 5 is a plot showing the effect of hydrogen pressure on lube viscosity index for isomerization of a Fischer-Tropsch wax over Pt/ZSM-48. Pour point (°C) on the abscissa is plotted against 700°F+ (371.1°C+) lube viscosity index (VI) on the ordinate. The dots represent 1000 psig (6996 kPa) hydrogen, the x's represent 500 psig hydrogen (3549 kPa), the filled triangles represent 300 psig (2170 kPa) hydrogen, and the open diamond represents 0 psia hydrogen (0 kPa, no hydrogen).

[0018] For the particular set of features described herein, working in the substantial absence of added hydrogen and at reduced hydrogen partial pressures results in increased catalyst activity and increased yield of desired product with little hydrocracking (as evidenced by the low C₁-C₄ gas yields in Figure 3).

DETAILED DESCRIPTION OF THE INVENTION

[0019] In Figure 1, line 10 indicates a source of paraffin feed. Most preferably the feed is derived from a Fischer-Tropsch hydrocarbon synthesis process, particularly one that is operated in a non-shifting mode with a cobalt or ruthenium based catalyst, preferably a cobalt containing catalyst.

[0020] The feed is forwarded to first catalytic dewaxing zone 16 via open valve 12 and line 13. Hydrogen, to the extent desired, is fed through line 25. At the same time a source of an oxygen containing gas, i.e., oxygen, air, oxygen enriched air or oxygen in suitable proportion with inerts such as nitrogen, from

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source 30, is fed to a second zone 18 via open valve 32 and line 34 where deactivated catalytic dewaxing catalyst is regenerated. Regeneration off gases are removed through open valve 24 and line 26.

[0021] The catalytically dewaxed product from zone 16 is removed via open valve 44 through lines 40 and 48 to distillation zone 50 where products are recovered, e.g., diesel in line 52 and lube base stock in line 54.

[0022] Upon deactivation of the catalyst in zone 16, valves 12 and 44 are closed, oxygen from source 30 is fed to zone 16 via open valve 38 and line 36. Regeneration off gases are removed through open valve 20 and line 22.

[0023] Similarly, when zone 16 is being regenerated, valve 12 is closed and paraffin feed is delivered to zone 18 for catalytic dewaxing via open valve 14 and line 15. Hydrogen to the extent desired is fed through line 27. Product is recovered in line 42 and fed via open valve 46 and line 48 to distillation zone 50.

[0024] The cyclic nature of the process is denoted by open valves 12, 44, 32, and 24 and closed valves 14, 46, 38 and 20, and then upon deactivation of catalytic zone 16 with open valves 14, 46, 38, and 20 and closed valves 12, 44, 32, 24, whereupon catalytic dewaxing takes place in zone 18 and the catalyst in zone 16 is regenerated.

[0025] Catalytic dewaxing of paraffin containing feeds, preferably feeds produced from syn gas using a non-shifting Fischer-Tropsch catalyst, is accomplished at relatively low hydrogen partial pressures without substantial effect on the life of a ZSM-48 catalyst. The dewaxing process is essentially an isomerization process in which some hydrogen will be produced indigenously.

[0026] The feed that is employed in this invention is a paraffin containing feed, preferably a feed that contains greater than 80 wt% n-paraffins, more

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preferably greater than 90 wt% n-paraffins, still more preferably greater than 95 wt% n-paraffins and still more preferably 98 wt% n-paraffins. The feed generally boils in the range 430°F+ (221.1°C+), preferably 450°F+ (232.2°C+), more preferably 450-1200°F (232.2-648.9°C) (minor amounts, e.g., less than about 10% of 1200°F+, or 648.9°C+, material may be present).

[0027] The feed is preferably low in unsaturates, that is, low in both aromatics and olefins. Preferably, the unsaturates level is less than 10 wt%, preferably less than 5 wt%, more preferably less than 2 wt%. Also, the feed is relatively low in nitrogen and sulfur, e.g., less than 200 ppm, preferably less than 100 ppm, such as less than 50 wppm of each. Where a Fischer-Tropsch derived feed is employed, there is no need to pre-sulfide the catalyst, and indeed, pre-sulfiding should be avoided.

[0028] Most preferably, the feed is the product of a Fischer-Tropsch reaction that produces essentially n-paraffins, and still more preferably the Fischer-Tropsch process is conducted with a non-shifting catalyst, e.g., cobalt or ruthenium, preferably a cobalt containing catalyst.

[0029] The catalyst employed in the catalytic dewaxing step comprises a molecular sieve with one dimensional pore structure and a metal dehydrogenation component. The molecular sieves include such as ZSM-23, ZSM-35, ZSM-22, SSZ-32, zeolite beta, mordenite and rare earth ion exchanged ferrierite, preferably a ZSM-48 catalyst, containing a metal dehydrogenation functionality, preferably supplied by the presence of platinum or palladium or both platinum and palladium, more preferably platinum. The catalyst may be sulfided or unsulfided and is preferably unsulfided when sulfur can negatively interfere with associated processes, such as a Fischer-Tropsch process.

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[0030] The molecular sieve catalyst support is described in J. Schlenker, et al, Zeolites, 1985, vol. 5, November, 355-358, hereby incorporated by reference. ZSM-48, in particular, is characterized by the X-ray diffraction pattern shown in Table 1 below. The material is further characterized by the fact that it exhibits a single line within the range of 11.8 ± 0.2 Angstrom units, i.e., $(11.8 \pm 0.2) \times 10^{-10}$ m. The presence of a single line at the indicated spacing structurally distinguishes ZSM-48 from closely related materials such as ZSM-12 (described in U.S. Patent No. 3,832,449) which has two lines, i.e., a doublet, at 11.8 ± 0.2 Angstrom units, $(11.8 \pm 0.2) \times 10^{-10}$ m, and high silica ZSM-12 (described in U.S. Patent No. 4,104,294) which also has a doublet at the indicated spacing.

Table 1
Characteristic lines of ZSM-48 (calcined, Na Exchanged Form)

d(A, 10^{-10} m)	Relative Intensity (I/I ₀)
11.8±0.2	S
10.2±0.2	W-M
7.2±0.15	W
4.2±0.08	VS
3.9±0.08	VS
3.6±0.06	W
3.1±0.05	W
2.85±0.05	W

[0031] The values were determined by standard technique, i.e., radiation was K-alpha doublet of copper, and diffractometer equipped with a scintillation counter. The peak heights, I, and the positions as a function of two times theta, where theta is the Bragg angle, were determined by a compactor. From these the relative intensities, $100 I/I_0$, where I_0 is the intensity of the strongest line or peak, and d(obs.), the interplanar spacing in A corresponding to the recorded

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lines were calculated. Table 1 gives the intensities in terms of the symbols W=weak, S=strong, VS=very strong, M=medium, and W-M=weak to medium (depending on the cationic form). Ion exchange of the sodium ion with other cations reveals substantially the same pattern with some minor shifts in interplanar spacing and variation in relative intensity. Other minor variations can occur depending on the silicon to aluminum ratio of the particular sample, as well as any subsequent thermal treatment.

[0032] ZSM-48 and methods for its preparation are described in U.S. Patent Nos. 4,375,573; 4,397,827; 4,448,675; 4,423,021; and 5,075,269. The method of preparation described in U.S. Patent No. 5,075,269 is particularly preferred, and is incorporated herein by reference. This method is for preparing a catalyst particularly suitable for the catalytic dewaxing process.

[0033] The zeolite, ZSM-48, and other utilizable zeolites, such as ZSM-23, ZSM-35, ZSM-22, SSZ-32, zeolite beta, mordenite and rare earth ion exchanged ferrierite, are usually employed with a dehydrogenation component in an amount of about 0.01 to 5.0 wt%, the component being manganese, tungsten, vanadium, zinc, chromium, molybdenum, rhenium, Group VIII metals such as nickel, cobalt, or the noble metals platinum and palladium. The noble metals are preferred components. Such component can be exchanged into the composition, impregnated thereon, or physically intimately admixed therewith. Such component can be impregnated in or onto the zeolite such as, for example, in the case of platinum, by treating the zeolite with a platinum metal-containing ion. Thus, suitable platinum compounds include chloroplatinic acid, platinous chloride and various compounds containing the platinum tetra-ammonia complex. Platinum and palladium are preferred hydrogenation components.

[0034] The compounds of the useful platinum or other metals can be divided into compounds in which the metal is present in the cation of the compound and

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compounds in which it is present in the anion of the compound. Both types of compounds which contain the metal in the ionic state can be used. A solution in which platinum metals are in the form of a cation or cationic complex, e.g., $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, is particularly useful.

[0035] Prior to its use, the ZSM-48 catalyst should be dehydrated at least partially. This can be done by heating to a temperature in the range of from about 100°C to about 600°C in an inert atmosphere, such as air, nitrogen, etc., and at atmospheric or subatmospheric pressures for between 1 and 48 hours. Dehydration can also be performed at lower temperature merely by placing the catalyst in a vacuum, but a longer time is required to obtain sufficient amount of dehydration. ZSM-48 is formed in a wide variety of particle sizes. Generally speaking, the particles can be in the form of a powder, a granule, or a molded product, such as extrudate having a particle size sufficient to pass through a 2 mesh (Tyler) screen (10 mm pore size) and be retained on a 400 mesh (Tyler) screen (0.038 mm pore size). In cases where the catalyst is molded, such as by extrusion, the crystalline silicate can be extruded before drying, or dried or partially dried and then extruded.

[0036] As in the case of many other zeolite catalysts, it may be desired to incorporate the ZSM-48 with a matrix material which is resistant to the temperatures and other conditions employed in the dewaxing process herein. Such matrix materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and/or metal oxides, e.g. alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates, sols or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the ZSM-48, i.e., combined therewith, which is active, may enhance the conversion and/or selectivity of the catalyst herein. Inactive materials suitably serve as diluents to

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control the amount of conversion in a given process so that products can be obtained economically and orderly without employing other means for controlling the rate of reaction. Frequently, crystalline silicate materials have been incorporated into naturally occurring clays, e.g., bentonite and kaolin. These materials, i.e., clays, oxides, etc., function, in part, as binders for the catalyst. It is desirable to provide a catalyst having good crush strength since in a petroleum refinery the catalyst is often subject to rough handling which tends to break the catalyst down into powder-like materials which cause problems in processing.

[0037] Naturally occurring clays which can be composited with ZSM-48 include the montmorillonite and kaolin families which include the sub-bentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays, or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

[0038] In addition to the foregoing materials, ZSM-48 can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix can be in the form of a cogel. Mixtures of these components can also be used. The relative proportions of finely divided crystalline silicate ZSM-48 and inorganic oxide gel matrix vary widely with the crystalline silicate content ranging from about 1 to about 90 percent by weight, and more usually in the range of about 2 to about 80 percent by weight, of the composite.

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[0039] In general, reaction conditions for dewaxing may vary widely even when the hydrogen partial pressures are maintained at low levels, e.g., 0 psig hydrogen. Thus, start of run temperatures may vary between about 550-650°F (288-343°C). End of run conditions can be defined by the nature of the product being produced, for example, when color specifications can no longer be met (an indication of catalyst deactivation), or when the pre-determined pour point can no longer be obtained, or the selectivity to isomerization is reduced as evidenced by an increase in methane yield due to hydrocracking. In general, however, end of run temperatures should be less than about 800°F (427°C), preferably less than about 750°F (399°C), more preferably less than about 725°F (385°C).

[0040] Catalyst deactivation is believed to be a result of coke formation on the surface of the catalyst, the coke covering or blocking access to the catalytic metal, as well as blocking the pores of the zeolite.

[0041] The catalyst may be regenerated by known methods including hot hydrogen stripping, coke removal by oxygen treatment or a combination of hydrogen stripping and oxygen treatment. (Figure 1 illustrates a process where oxygen treatment is used to regenerate the catalyst).

[0042] Briefly, hydrogen stripping can be carried out with hydrogen or a mixture of hydrogen and an inert gas such as nitrogen, at isomerization reaction temperatures for a period of time sufficient to allow the catalyst to regain at least about 80%, preferably at least about 90% of its original lined out activity. Oxygen treatment can be carried out at calcining conditions, e.g., using air at temperatures from about 500°C to 650°C, again for a period of time sufficient to allow the catalyst to regain at least about 80%, preferably at least about 90% of initial lined out activity after subsequent reduction.

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[0043] In general, where hydrogen is present, other gases may be present, too, and will not interfere with the reaction. Such other gases may be nitrogen, methane, or other light hydrocarbons (that may be produced during the reaction). Total pressure may range up to 2000 psia (13790 kPa), preferably 100-2000 psia (690-13790 kPa), more preferably 150-1000 psia (1034-6895 kPa), still more preferably 150-500 psia (1034-3448 kPa). Hydrogen can make up 50-100% of total gas, preferably 70-100%, more preferably 70-90%. At the low hydrogen partial pressures recited herein, small amounts of olefins and aromatics may form when the isomerization is carried out in the substantial absence of hydrogen; and hydrofinishing, at well known conditions, may be necessary to remove these components.

[0044] , The liquid hourly space velocity is generally between about 0.1 and about 10, and preferably is generally between about 0.5 and 4 volume of feed per volume of catalyst per hour. The hydrogen to feed (where hydrogen is used) ratio is generally between about 100 (17.8 liter/liter) and about 10,000 (1781 liter/liter), and preferably between about 800 (142.5 liter/liter) and about 4,000 (712.4 liter/liter) standard cubic feet (scf) of hydrogen per barrel of fuel.

[0045] Alpha Value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst and provides a relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). The value is based on the activity of a silica-alumina cracking catalyst taken as an Alpha of 1 (rate constant = 0.016 sec^{-1}). The test for Alpha Value is described in U.S. Patent No. 3,354,078 and in the Journal of Catalysis. vol. 4, p. 527 (1965); vol. 6, p. 278 (1966); and vol. 61, 395 (1980), each incorporated herein by reference. The Alpha Value of the catalyst prior to metal loading is preferably in the range of about 10 to about 50.

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[0046] In the following examples, a Fischer-Tropsch wax having the properties shown in Table 2 below was used as feedstock for all isomerization reactions.

Table 2

<u>Fischer-Tropsch Wax</u>	
Pour point, °C	82
IBP-700°F (371.1°C) (<C ₂₄), wt%	3
700°F (371.1°C)-1100°F (593.3°C) (C ₂₄ -C ₆₀),	89
1100°F+ (593.3°C+) (C ₆₀ +), wt%	8

[0047] In all examples the catalyst was alumina bound (35wt%), ZSM-48 crystals containing 0.6 wt% platinum (Pt dispersion based on hydrogen absorption: H/Pt=1.03).

[0048] Wax isomerization was performed using a micro unit equipped with a three zone furnace and a downflow trickle bed tubular reactor (0.5 inch ID). The unit was heat traced to avoid freezing of the high melting point feed wax. The catalyst extrudates were crushed and sized to 60-80 mesh (0.180-0.250 mm). The reactor was loaded with a mixture of 15cc sized catalyst and 5cc of 80-120 mesh (0.125-0.180 mm) sand, which was then dried and reduced at 400°F (204.4°C) for one hour at one atmosphere, 240 cc/min hydrogen flow. Isomerization was conducted at 1.0 hr⁻¹ LHSV and at pressures indicated. When hydrogen was used as a co-feed, the hydrogen/feed ratio was 5000 scf/bbl (890.5 liter/liter). In cases where no hydrogen was used, reactor pressure was maintained at 1000 psig (6996 kPa). Isomerization reactions were started with feed at an initial temperature of 665°F (351.7°C) and hydrogen (where used) as noted. Material balances were carried out overnight for 16-24 hours after 8-12 hour line out period. Reactor temperature was gradually changed to vary pour point.

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[0049] Off gas samples were analyzed by GC using a 60 m DB-1 (0.25 mm ID) capillary column with FID detection. Total liquid products (TLP's) were weighed and analyzed by simulated distillation (M1567 or D2887). TLP's were distilled into IBP-330°F (initial boiling point-165.6°C) naphtha, 330-700°F (165.6-371.1°C) distillate, and 700°F+ (371.1°C+) lube fractions. The lube fractions were analyzed further by simulated distillation (simdis) to ensure accuracy of the actual distillation operations. Pour point and cloud point of 700°F+ (371.1°C) lubes were measured using D97 and D2500 methods, respectively; viscosities were determined at both 40°C and 100°C according to D 445-3 and D 445-5 methods, respectively.

[0050] Hydrogen pressure was found to affect substantially both catalyst activity and product selectivity. Upon decreasing hydrogen pressure, catalyst activity increased, e.g., 25-30°F (14-16.7°C) where hydrogen pressure was reduced from 1000 psig (6996 kPa) to 300 psig (2170 kPa). Similarly, selectivity to lube base stock (700°F+, 371.1°C+) increased with decreasing hydrogen pressure. Figure 2 shows that lube yield was higher at lower hydrogen pressure. A maximum lube yield (app. 90% at -12°C pour point) was obtained in the substantial absence of added hydrogen. At the same time, the yields of lighter by-products, that is, light gas (C₁-C₄), naphtha, and distillate were decreased with decreasing hydrogen pressure. Thus, the increased lube yield is clearly a function of increased selectivity for the catalyst.

[0051] By virtue of the enhanced selectivity, there appears to be lower rates of cracking side reactions. As hydrogen pressure is reduced, catalyst activity increases and a lower reaction temperature is required to achieve a target, or pre-determined, lube pour point. Both factors, substantial absence of hydrogen and lower reaction temperature should reduce cracking, such as hydrogenolysis and

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thermal or catalytic cracking. Hydrogenolysis in the absence of hydrogen should be negligible. See Figure 3 regarding gas yields.

[0052] Lube base stock viscosity at a given, or pre-determined, pour point was higher, too, at lower hydrogen pressure, and reached a maximum with no hydrogen as co-feed; i.e., 0 kPa (zero psia) hydrogen. For example, at -20°C pour point, the 700°F+ (371.1°C+) lube base stock obtained without co-feeding hydrogen had a KV at 100°C of 7.7 cSt which is significantly higher than the 6.7 cSt base stock obtained with a 1000 psig (6996 kPa) hydrogen pressure, as shown in Figure 4. Hence, it is especially surprising that, using the process of the invention, the viscosity of the feed is better preserved, while at the same time the pour and cloud point is decreased.

[0053] Viscosity and viscosity index are two key properties of lube base stocks. Figure 5 shows that lowering hydrogen partial pressure, even to 0 psia (0 kPa), essentially had no effect on viscosity index of the lube base stocks.

[0054] Table 3 below shows the results of isomerizing a Fischer-Tropsch wax, i.e., catalytic dewaxing in the substantial absence of added hydrogen. "MB" refers to material balance. TBP x% indicates a final boiling temperature, at which x wt% light fraction of a hydrocarbon sample boils.

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Table 3

MB Number	1	2	3	4
Time on Stream, Days	62.5	64.5	65.6	66.6
Temperature, °F	630	625	620	620
Temperature, °C	332.2	329.4	326.7	326.7
Pressure, psig	1000	1000	1000	1000
Pressure, kPa	6996	6996	6996	6996
LHSV, hr ⁻¹	1.0	1.0	1.0	1.0
WHSV, hr ⁻¹	2.3	2.2	2.2	2.2
H ₂ @ inlet, scf/bbl	0	0	0	0
H ₂ , Hydrocarbon Feed, l/l	0	0	0	0
Product Yield, wt% Feed				
C ₁ -C ₄ Gas, wt%	2.8	1.2	0.6	0.4
C ₅ -330°F Naphtha, wt%	7.5	3.9	1.4	0.4
330-700°F Diesel, wt%	18.0	12.0	8.0	6.0
700°F+ Lube Yield, wt%	72.0	83.0	90.0	93.2
Total HC, wt% on Feed	100.3	100.1	100.1	100.0
Lube Properties				
Isolated Yield, wt%	70.8	82.3	86.0	88.4
KV @ 40°C, cSt	40.1	38.7	40.6	41.4
KV @ 100°C, cSt	7.39	7.44	7.85	8.10
Viscosity Index	152.1	162.1	168	173.5
Pour Point, °C D97	-42	-33	-12	3
TBP 5%, °F by D2887	770	779	798	838
TBP 5%, °C by D2887	410.0	415.0	425.6	447.8
TBP 50%, °F	913	924	923	947
TBP 50%, °C	489.4	495.6	495.0	508.3
TBP 95%, °F	1044	1050	1042	1070
TBP 95%, °C	562.2	565.6	561.1	576.7
MB Closure, wt%	100.0	100.0	100.0	100.2

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CLAIMS:

1. A catalytic dewaxing process which comprises reacting a paraffin containing feed stock over a catalyst comprising a molecular sieve with a one dimensional pore structure having an average diameter of 0.50 to 0.65 nm, and a metal dehydrogenation component, at dewaxing reaction conditions and in the substantial absence of added hydrogen.
2. The process of claim 1 wherein the catalyst deactivation rate, as measured by temperature increase required to meet a predetermined pour or cloud point (TIR) is less than 25°F/year (14°C/year).
3. The process of claim 1 or claim 2 wherein the hydrogen partial pressure is less than about 100 psig (791 kPa).
4. The process of any of the preceding claims wherein the hydrogen partial pressure is less than about 70 psig (584 kPa).
5. The process of any of the preceding claims wherein the paraffin containing feed stock contains greater than 80 wt% n-paraffins and boils in the range above 430°F (221.1°C).
6. The process of any of the preceding claims wherein the dehydrogenation component is platinum or palladium.
7. The process of any of the preceding claims wherein the process comprises a cyclic catalytic dewaxing-catalyst regeneration process wherein catalyst is provided in a first reaction zone and a second reaction zone, the paraffin containing feed stock is dewaxed in the first reaction zone for a pre-

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determined period after which the paraffin containing feed is transferred to the second zone for dewaxing at reaction conditions, and catalyst in the first zone is regenerated.

8. The process of claim 7 wherein dewaxing occurs in the second zone for a pre-determined period after which the paraffin containing feed is transferred to the first reaction zone wherein dewaxing occurs over the regenerated catalyst, and the catalyst in the second zone is regenerated.

9. The process of claim 7 or claim 8 wherein catalyst regeneration is effected by hydrogen stripping or oxygen treatment.

10. The process of any of the preceding claims wherein the product of the catalytic dewaxing process is a lube base stock or a diesel range material.

11. The process of any of the preceding claims wherein the product is subjected to hydrofinishing.

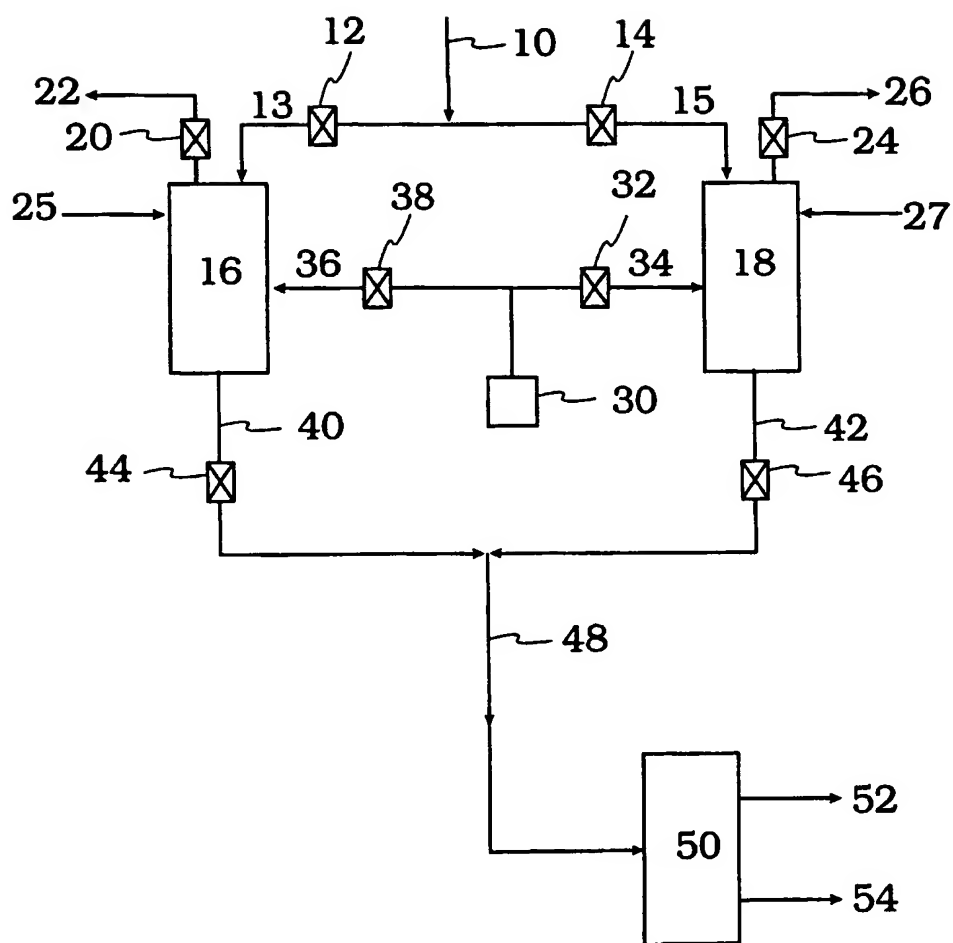
12. The process of any of the preceding claims wherein the molecular sieve is selected from the group consisting of ZSM-23, ZSM-35, ZSM-48, ZSM-22, SSZ-32, zeolite beta, mordenite, rare earth ion exchanged ferrierite and mixtures thereof.

13. The process of claim 12 wherein the molecular sieve is ZSM-48.

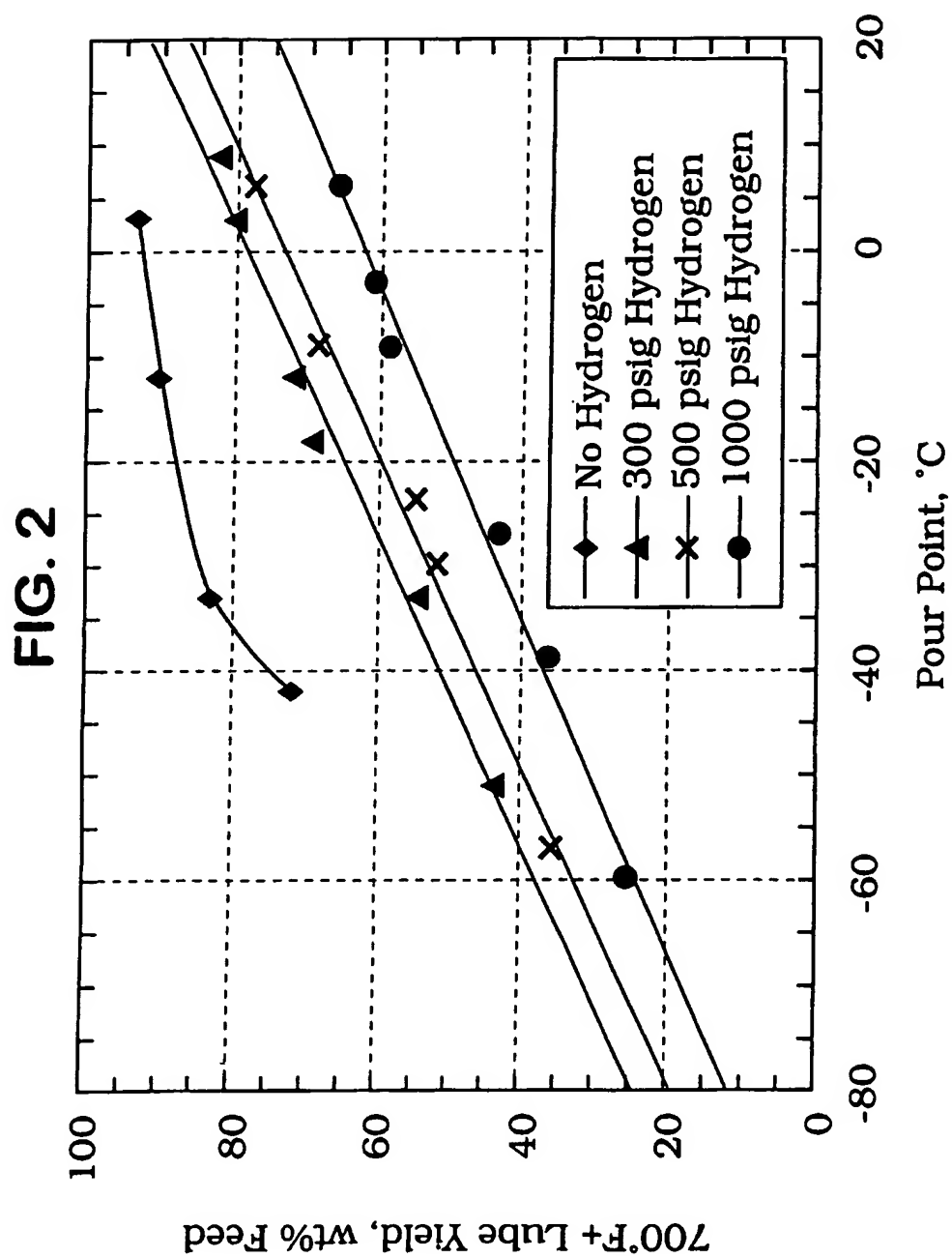
14. Use of the process of any of the preceding claims to (1) decrease the pour point or cloud point, or both, and (2) preserve the viscosity of a paraffin containing feed stock.

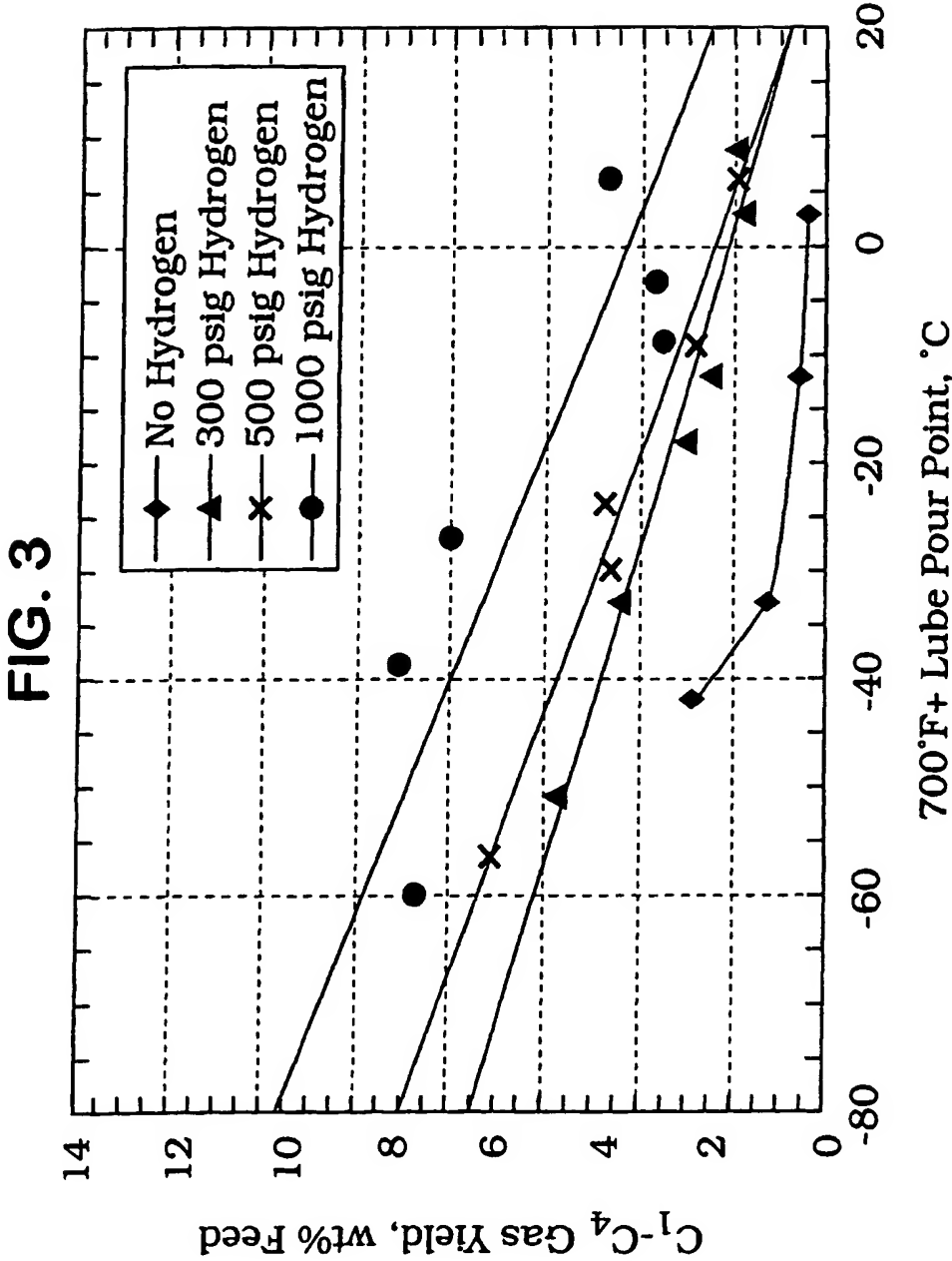
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FIG. 1

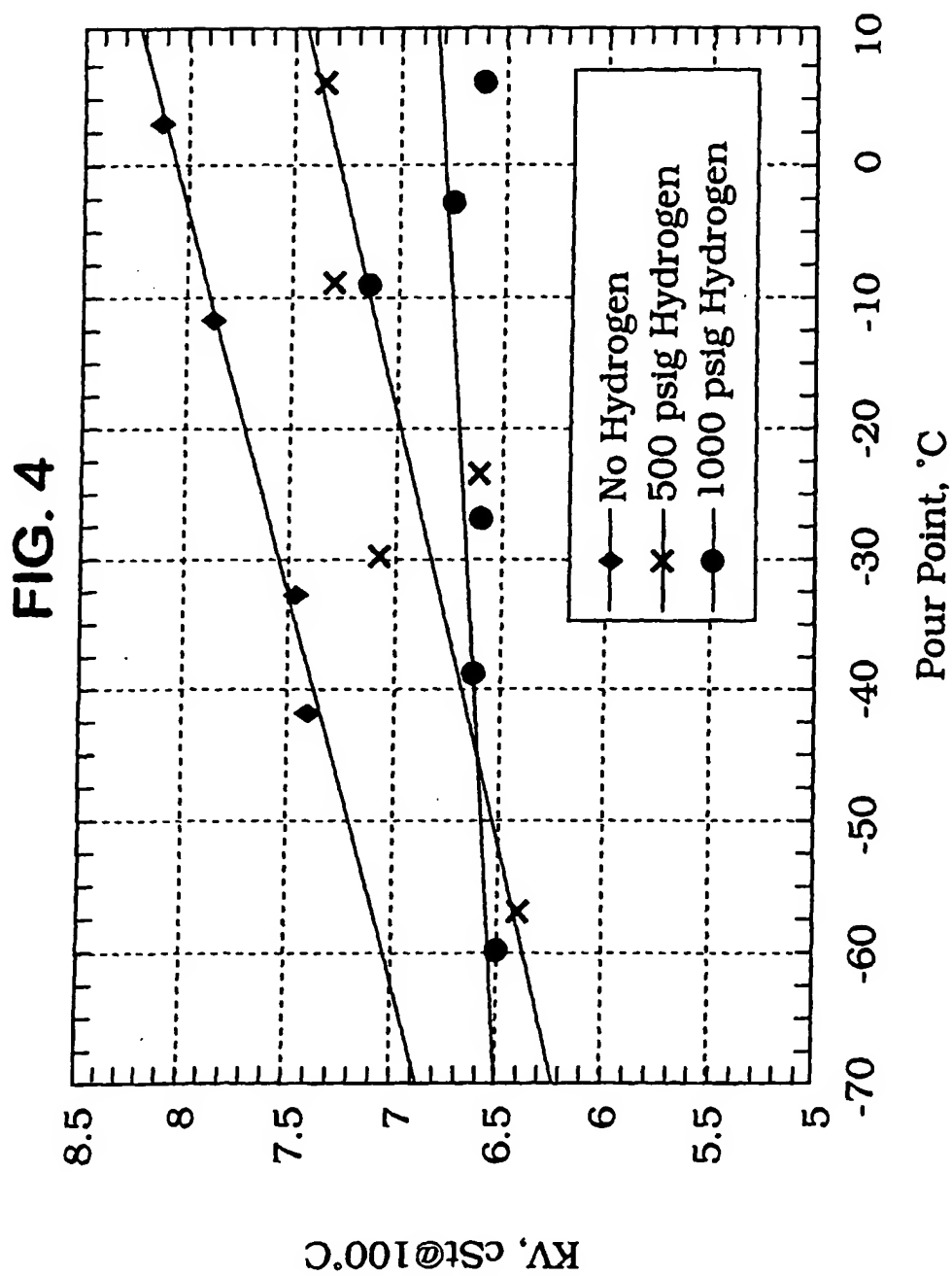


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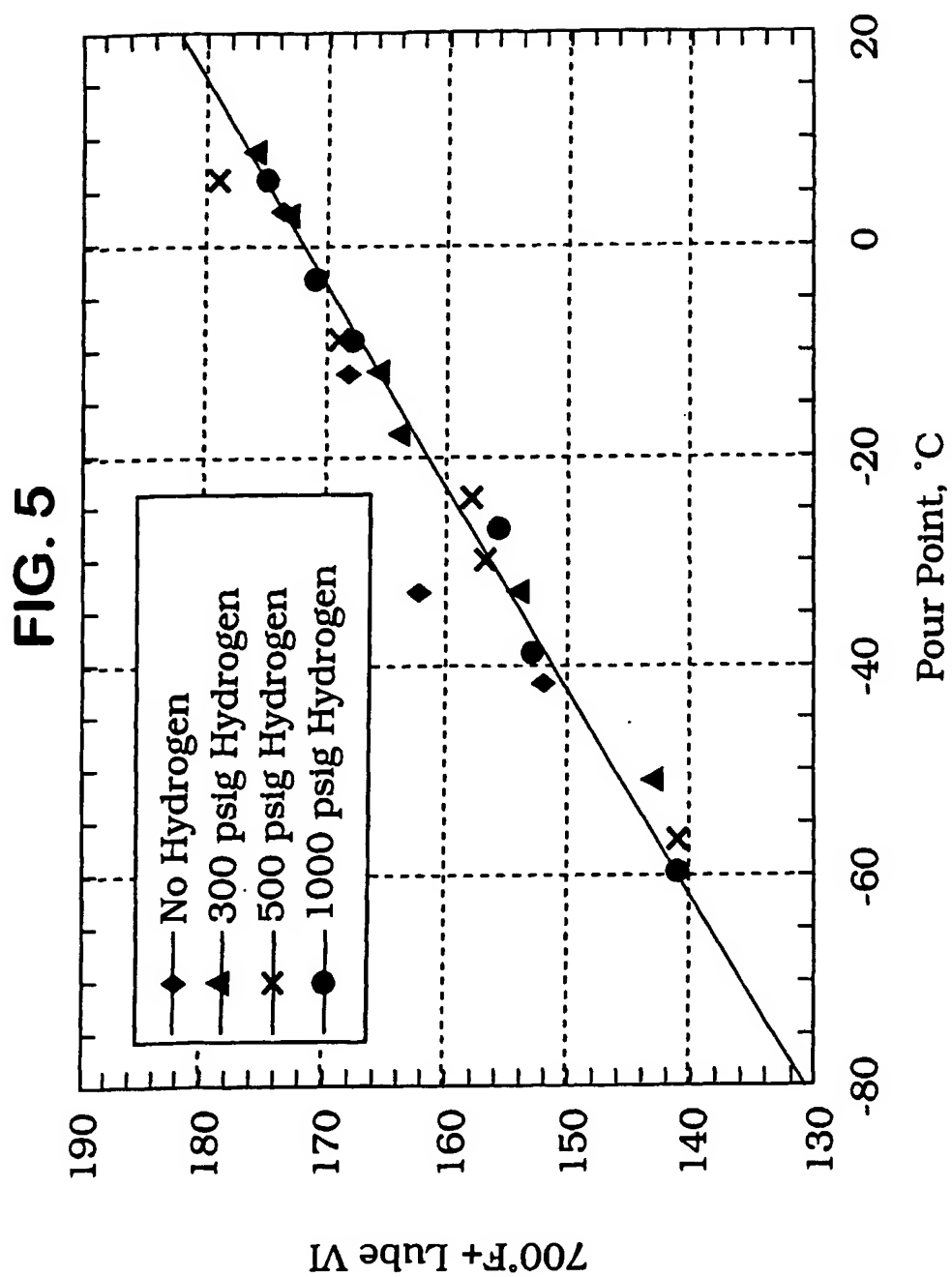




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INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US 03/31742

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C10G45/64 C10G45/62 C10G29/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, API Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 419 220 A (LAPIERRE RENE B ET AL) 6 December 1983 (1983-12-06) claims 1,7-9 column 2, line 10-13,49-58 column 6, line 50-60 column 7, line 10-16,50-56 ---	1-14
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

 European Patent Office, P.B. 5618 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

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INTERNATIONAL SEARCH REPORT

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